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J. Billingsley

JULIE BILLINGSLEY
TEAM LEADER EXAMINATION
SUPPORT AND SALES

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Solvents based on salts of aryl acids

Inventors: Stewart A. Forsyth, Douglas R. MacFarlane and Jonathan Upfal

Field of Invention

This invention relates to the application of salts of acids with aryl functionality as solvents or additives for dissolving, digesting, extracting and isolating materials from natural sources such as biomass. Properties such as low melting points, chemical and thermal stability and the ability to dissolve a wide range of aromatic compounds are of particular importance for the intended applications. Other properties such as surfactant behaviour and possible catalytic ability may also be important aspects of these solvents.

Background of invention

The conventional wood pulping method known as the kraft alkali process has a number of drawbacks. These can be inferred from consensus criteria as to what would constitute superiority in any proposed alternative, usually referred to collectively as "organosolv" pulping processes (adapted from summary of Worster 1974; Palenius 1987; Franzreb 1989; Leopold 1993; Schroeter 1993 in "Organosolv Pulping: a review and distillation related to peroxyacid pulping" PhD thesis prepared by Esa Muurinen, University of Oulu, Finland, 2000):

The novel pulping process should

- Manage suitably prepared hardwood, softwood and herbaceous raw materials
- Not degrade cellulose and dissolved hemicelluloses
- Not require higher temperatures, pressures or pulping times than are usual in kraft and sulphite pulping
- Utilize known and tested engineering methods and equipment already perfected for conventional kraft pulping, wherever possible

- Have an optimal size smaller than that of a typical kraft mill.

In addition, the resulting pulp should

- Be at least equal to the quality of kraft pulp
- Be readily bleachable without chlorine
- Offer high yield
- Be directly substitutable for kraft pulp by current end-users
- Allow valuable by-products to be recovered.

Finally, the process should

- Have efficient and simple chemical recovery systems
- Close the chemical cycle of the process, with little or no make-up chemical consumption
- Have low specific energy consumption
- Avoid malodorous emissions by being totally sulphur free
- Permit complete recovery of process water with minimal discharge
- For occupational health and safety, product residue, environmental, and other regulatory and public policy requirements, employ known chemicals that have negligible or low human and environmental toxicity, be non-flammable and non-explosive
- Facilitate economic, environmental and other efficiencies in existing conventional kraft pulping mills, if possible

Apart from investigations into such "organosolv" alternatives to the conventional kraft process in the production of paper pulp, considerable efforts have been expended *in parallel* over recent decades to create novel processes, for example utilizing enzymatic breakdown or concentrated mineral acids, to obtain fermentable sugars (and lignin) from the enormous volumes of waste lingo-cellulostic biomass that is currently plowed-in, burnt or discarded. The derived sugars are intended to provide the feedstock for conversion into a renewable source of greenhouse gas neutral liquid fuels such as ethanol, or other valuable industrial and fine chemicals. However, both the enzymatic and concentrated acid approaches to the processing of ligno-cellulostic

biomass pose technical hurdles that have prevented any significant commercial adoption to date, as is the also case with "organosolv" pulping in general.

However, amongst the many prospective chemicals that have been evaluated to form the basis of an "organosolv" alternative to kraft pulping, the hydrotropic pulping method that employs sodium xylenesulphonate, as taught by McKee (Can. Patent 631,051), stands out for the following reasons:

- Penetration of sodium xylenesulphonate into the wood chips or fibre is twice as rapid as in the kraft process
- Sodium xylenesulphonate is neutral, odourless and non-volatile
- Sodium xylenesulphonate has low to negligible toxicity in humans
- Air oxidation of the cellulose does not lower the pulp yield
- The concentration of sodium xylenesulphonate does not decrease during the pulping cycle
- The pulp can be bleached with less chemicals than kraft
- Sodium xylenesulfonate is a selective delignifying agent and no sugars are present in the spent pulping liquor, which can be reused until it is saturated with lignin.
- The process requires less equipment compared to a kraft mill
- Water consumption is low
- Energy consumption is less
- By-products can be recovered
- The process if free of odours and aqueous effluents
- Lignin can be precipitated by diluting the spent liquor with water; the liquor is then returned to its' original concentration by evaporation.

Hydrotropic chemicals are concentrated salt solutions that dissolve more of a slightly soluble material, particularly aromatics, than pure water does, offering up to 100 to 500 times the solubility of pure water at comparable temperatures. As instanced by McKee, one liter of a 30 percent solution of the hydrotrope sodium xylenesulphonate will, over time, dissolve several hundred grams of lignin from wood chips immersed in the solution at the appropriate temperature. And since the sodium xylenesulphonate is recovered unchanged following precipitation of saturated lignin in solution and

evaporative re-concentration of the dilute liquor, McKee claims that, in addition to its' solvation properties, sodium xylenesulphonate exerts catalytic effects that result in hydrolysis of chemical bonds within the lignin present in the biomass that further facilitates the dissolution of lignin.

Ionic liquids are salts with low melting points.[1-7] Ionic liquids have been used as solvents for a wide range of solvent applications.[8-10] The successful use of ionic liquids as solvents has been demonstrated for a wide range of organic reactions including acid catalysis, transition metal catalysis and biotransformations.[11-13] Specific features that make ionic liquids attractive include their lack of vapor pressure, ability to dissolve a wide range of organic and inorganic compounds and the versatility of their chemical and physical properties.

The versatility of ionic liquids is exemplified by the ability to 'tune' or 'tailor' ionic liquids to any given purpose. For example; by altering the combination of cations and anions, it is possible to adjust the solvent properties to meet desired process criteria. Interactions between ionic liquid solvents, substrates, active species and products significantly influence the viability and efficiency of solvent based processes. A wide spectrum of different physical and chemical properties of ionic liquids has been exploited where specific solvent characteristics are required or advantageous. Several examples of 'task-specific' ionic liquids include, hydrophobicity for dehydration reactions,[14] acidicity or basicity for dual role as solvent and catalyst,[15-17] chirality for solvent induced stereospecificity,[18,19] and functionalised ions that enhance the solubility of metal ions or sugars.[20,21]

For the intended purpose of the invention, namely treatment of biomass to yield commercially valuable cellulostic fibre, sugars, other valuable chemicals and lignin by-product, the advantage of ionic liquid salts of acids with aryl functionality - of which xylenesulphonic acid may be taken as the prototype acid - as solvents or additives compared to either conventional kraft pulping, or molecular solvents such as ethanol, or organic acid alternatives, lies in their superior solvating power, catalytic functionality, ease of handling and, in selected cases, low toxicity, amongst other attractive properties.

Description of invention

The solvents in this invention are primarily, but not restricted to, salts of arylsulfonic acids. **Figure 1** shows the arylsulfonate species that form the anion component of the ionic solvents. Other anions included in the broader scope of the solvents in this patent include arylcarboxylate, arylphosphinate, arylphosphate and arylsulfate. The later two typically have lower chemical and thermal stability but may have desirable solvency properties for some applications.

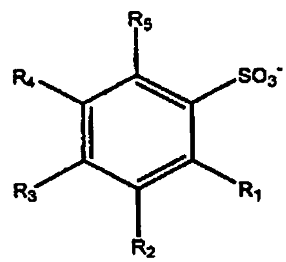
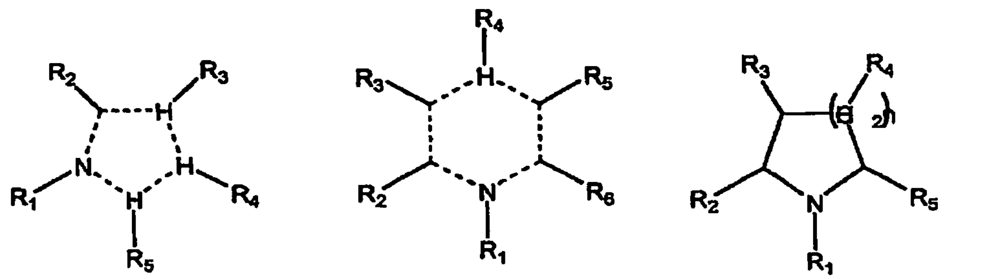


Figure 1 *Arylsulfonate anions*

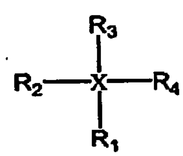
In this structure R_1, R_2, R_3, R_4, R_5 can be hydrogen, alkyl (including but not limited to methyl, ethyl, dodecyl), alicyclyl, aryl (including but not limited to benzyl and naphthyl), aralkyl, alkylaryl, heteroaryl, halogeno, haloaryl, sulfonate (these dianions may be partially or fully neutralised). The aromatic functionality of the arylsulfonate anion may also include any hetero-atoms, branched and/or ring fragments with the substituent promoting the solvent properties and/or physical properties of the corresponding solvent.

The cation component (**Figures 2 and 3**) of the solvent may consist of inorganic elements such as rare earth metals, organic cations such as imidazolium, triazolium, pyrazolium, pyridinium, pyrrolidinium, piperidinium, ammonium, phosphonium, sulfonium where the substituents consist of hydrogen, aliphatyl, alicyclyl, aryl, aralkyl, alkylaryl, heteroaryl, haloaryl. Also other inorganic cations capable of providing improved solvent properties and/or physical properties.



Imidazolium and triazolium — Pyrazolium and pyridinium — Pyrrolidinium and piperidinium

Figure 2 *Organic cations, H = carbon, nitrogen, oxygen or sulfur atoms. Dotted lines are single or double bonds.*



Ammonium, phosphonium and sulfonium

Figure 3 *Organic cations, X = Nitrogen, phosphorus or sulfur atoms*

The salts, which are the subject of this invention, are generally liquids at some temperature below 250°C either in their pure state or when mixed with one or more other salts which may also be the subject of this invention or known salts (other ionic liquids).

In the liquid state such salts offer special solvating properties for a number of commercially important materials. One such material is lignin, which may be extracted from wood pulp by the ionic solvents that are the subject of this invention.

The ionic solvents that are the subject of this invention may also include a further component which is a molecular solvent including water, ethanol, toluene and other solvents well known in the field of chemistry. Commonly used acids and bases may

also be added to this mixture for simple pH management of optimal conditions or other advantageous effect. Such additional solvent components may be present at weight percentages from 0.01% - 90%. Alternatively, the ionic liquids that are the subject of this invention may be added to the composition of conventional kraft alkali liquors to facilitate and accelerate removal of lignin.

These ionic solvents also display high electrochemical stability compared to conventional electrolytes. Typically large electrochemical windows are observed using cyclic voltammetry. Ionic solvents of this type are therefore of interest as electrolytes, or ionic additives, for electrochemical applications such as electrowinning technologies. Any metal salt, including; copper, titanium, and aluminium, that can be dissolved in the ionic solvent and electrochemically reduced is potentially recoverable in the metallic form.

Synthesis of novel materials

Example 1: 1-ethyl-3-methylimidazolium xylenesulfonate (EmImXS) is prepared by metathesis of sodium xylenesulfonate and 1-ethyl-3-methylimidazolium bromide.

EmImXS is a useful liquid salt for the extraction of lignin from pulp at temperatures around 150 °C in a solvent mixture which contains water and some residual sodium xyelenesulfonate.

Example 2: Trihexyltetradecylphosphonium xylenesulfonate $P_{66614}XS$ is prepared using an ion-exchange column loaded with xylenesulfonate anions and passing a solution of trihexyltetradecylphosphonium chloride through several times until complete exchange is indicated by the lack of chloride ions in the eluent. ^{1}Hnmr ($CDCl_3$) δ 0.85-0.95 (m, 12H, CH_3), 1.20-1.35 (m, 48H, CH_2), 1.40-1.60 (m, 14H, P-CH_2 & Ar-CH_3), 6.90-7.30 & 7.60-7.90 (m, 3H, CH). Electrospray Mass Spec: ES^+ 483 [$P_{66614}{}^+$] m/z. ES^- 185 [XS^-] m/z.

P_{66614}~~DDBS~~XS displays excellent thermal stability at 150 °C. Thermogravimetric analysis indicates the loss of less than 0.2% volatile material during 4 hours at this

temperature. Thermal decomposition temperature was calculated using the step-tangent method to be 310°C.

Example 3: Tetrabutylammonium dodecylbenzenesulfonate N_{4444}DDBS is prepared by neutralising an aqueous solution of dodecylbenzenesulfonic acid with tetrabutylammonium hydroxide and removing water by evaporation.

Example 4*N*-butyl-*N*-methylpyrrolidinium 4-hydroxybenzenesulfonate is prepared directly in one-pot by alkylating *N*-butylpyrrolidine with the methyl ester of 4-hydroxybenzenesulfonic acid.

Use of novel materials

Example 5: An extraction process is carried out as followsA reaction vessel is charged with a solution of ionic liquid based solvent. Biomass such as wood chips or hebaceous material are added to the vessel. The mixture is heated and stirred for several hours. Solid cellulosic material is filtered and prepared for pulping to paper. Dilution of the filtrate after repeated digestion cycles with water precipitates lignin, which is collected. Distillation of the filtrate affords various volatile chemicals. The ionic liquid based solvent is recycled to the beginning of the process.

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